



## Oleogels of virgin olive oil with carnauba wax and monoglyceride as spreadable products

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**SUMMARY:** The oleogels of virgin olive oil with carnauba wax and monoglyceride were prepared to determine the most suitable spreadable product. The oil binding capacities of monoglyceride oleogels were higher than those of the carnauba wax oleogels. There was no true crystalline structure with carnauba wax at 3%. Although the highest solid fat content was in the 10% monoglyceride oleogel (9.38%), it was 12.15% in the commercial breakfast margarine at 20 °C. The peak melting temperature of the margarine was 47.11 °C, and among all oleogels, monoglyceride oleogel at 7% addition had the closest value (48.70 °C). The melting enthalpies of the oleogels ranged from 1.25 to 103.97 J·g<sup>-1</sup>, while it was 94.19 J·g<sup>-1</sup> for the margarine sample. The firmness and stickiness values were usually lower in the oleogel samples than those of the margarine sample. There was no significant change in the texture parameters during storage, indicating good structural stability. The polarized light microscopy pictures revealed rod-like crystals for carnauba wax and rosette-like aggregates for monoglyceride oleogels. X-ray diffraction patterns of the samples have revealed a  $\beta'$ -type polymorphic structure for the oleogels. These oleogels can be used in a spreadable, breakfast margarin-like product to promote new consumption habits for this healthy oil.

**KEYWORDS:** *Carnauba wax; Monoglyceride; Oleogel; Storage; Virgin olive oil; X-ray diffraction*

**RESUMEN:** *Oleogeles de aceites de oliva virgen con cera de carnaúba y monoglicéridos como productos para untar.* Se prepararon oleogeles de aceites de oliva virgen con cera de carnaúba y monoglicéridos para encontrar el producto más adecuado para untar. La capacidad de unión de aceites de oleogeles de monoglicéridos fue más alto que el de los oleogeles de cera de carnaúba. No hubo ninguna estructura cristalina verdadera con cera de carnaúba al 3%. Aunque el mayor contenido de grasa sólida fue con el 10 % de oleogeles de monoglicérido (9,38 %), fue del 12.15 % en el de margarina comercial a 20 °C. La temperatura pico de fusión de la margarina fue 47,11 °C, y entre todos los oleogeles, los de monoglicérido al 7 % tuvo el valor más próximo (48,70 °C). La entalpía de fusión de los oleogeles estaban en el rango entre 1,25 y 103,97 J·g<sup>-1</sup>, mientras que fue de 94,19 J·g<sup>-1</sup> para la muestra de la margarina. Los valores de firmeza y adherencia fueron por lo general más bajas en las muestras de oleogeles que en la muestra de margarina. Mientras que no hubo cambios significativos en los parámetros de textura durante el almacenamiento, indicando una buena estabilidad estructural. Las imágenes de microscopía de luz polarizada reveló cristales en forma de varilla de cera de carnauba y agregados en forma de rosetones para los oleogeles monoglicéridos. Los diagramas de difracción de rayos X de las muestras reveló tener estructura polimórfica estándar tipo- $\beta'$  para los oleogeles. Estos oleogeles pueden ser productos tipo margarina untable para el desayuno y proporcionar nuevos hábitos de consumo saludable.

**PALABRAS CLAVE:** *Aceite de oliva virgen; Almacenamiento; Cera de carnaúba; Difracción de rayos X; Monoglicérido; Oleogel*

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## 1. INTRODUCTION

Organogels are three-dimensional, self-standing, thermo-reversible, anhydrous, viscoelastic gels created by adding small molecular weight organogelators and/or polymeric gelators, which can self-assemble themselves into gel networks via non-covalent interactions, into an organic phase and mixing and sometimes heating and cooling to entrap the liquid phase. If the organic phase is an edible oil, the resulting gel can also be called an 'oleogel' instead of 'organogel' (Toro-Vazquez *et al.*, 2007; Rogers, 2009; Bot *et al.*, 2009; Co and Marangoni, 2012). The oleogels are interesting products which are currently being used in structuring edible oils for margarine and shortening-like products, emulsion-based products, and in other processed food applications (bakery, processed meat, ice cream and dairy, confectionary and edible films). Since organogelation does not cause any change in the fatty acid saturation level or isomer forms, it could be advantageous for maintaining the health promoting features of the liquid oil intact in the oleogel. At the same time, the crystalline structure developed through organogelation can supply the proper rheological properties such as texture formation, creaminess, softness, aeration, plasticization, mouth feel etc. for different food applications (Dassanayake *et al.*, 2011; Co and Marangoni, 2012; Stortz *et al.*, 2012; Toro-Vasquez *et al.*, 2013).

Various edible liquid oils and organogelator molecules have been used to prepare oleogels for different purposes (Co and Marangoni, 2012; Stortz *et al.*, 2012). Among others, virgin olive oil (VOO) is a preferred one for organogel production since it is a virgin, aromatic and healthy oil (Boskou, 1996). Similarly, chemically different organogelators have been used and compared for organogel properties. As basic requirements, organogelators for oleogel production must be at least safe, edible, efficient, common and cheap (Co and Marangoni, 2012; Patel *et al.*, 2013; Toro-Vasquez *et al.*, 2013; Patel *et al.*, 2014). The rheological properties of olive oil-monoglyceride organogels under deformations were investigated, and the oiling out effect of shearing was approved (Ojijo *et al.*, 2004). The analyses of the morphology of olive oil-monoglyceride organogels have revealed needle-like crystals with 5–15 µm in length (Kesselman and Shimoni, 2007). Olive oil organogel was also prepared with a cross-linked  $\beta$ -lactoglobulin stabilized oil-in-water emulsion by Mezzenga (2011). It was also shown that impurities in virgin olive oil cause indigeneous cross-linking with protein to prevent rehydration of the protein. Similarly, olive oil-water emulsions containing mono- and di-glycerides and cocoa butter were prepared and compared with margarine for rheology (Lupi *et al.*, 2011). In a more recent study (Lupi *et al.*, 2012), olive oil organogels with mono/diglycerides and Myverol

at different concentrations were compared. It was shown that the desired macroscopic properties can be adjusted according to the organogelator concentration, whereas dynamic moduli can be changed by modifying saturated to unsaturated fatty acid ratios of the mixture. The same research group (Lupi *et al.*, 2013a) investigated the rheology of olive oil-polycosanol organogels at different addition levels and temperatures. It was shown that the onset of the crystallization temperature increases non-linearly with polycosanol concentration, and a fractal model was developed for storage modulus as a function of organogelator concentration. Recently (Lupi *et al.*, 2013b), an organogel based on olive oil-polycosanol was developed for the delivery of ferulic acid as the active agent. *In vitro* digestion tests have proven the good delivery and release ability of the gel.

Saturated monoglycerides have been studied as organogelator agents (Battle *et al.*, 2007; Rush *et al.*, 2008; Da Pieve *et al.*, 2010 and 2011; Toro-Vasquez *et al.*, 2013) in different oils. Similarly, carnauba wax was used as an organogelator in salad oil and studied in detail (Dassanayake *et al.*, 2009) and in soybean oil, only a minimum gel forming concentration was determined as 3-5% by weight (Hwang *et al.*, 2012). From the above reviewed literature, it was determined that more studies on VOO with different organogelators for specific purposes are needed. In this study, we formed oleogels of VOO with carnauba wax (CW) and monoglyceride (MG) at different addition levels to find the most similar one to the commercial breakfast margarine (BM). Addition levels of 3, 7 and 10% were selected based on pre-experiments to fit the objective. In order to determine the level of similarity, thermal and textural characterization of the samples were completed together with some other physical measurements and morphological characterizations. Also, a three months storage study was carried out at room and refrigerator temperatures for texture and oxidation stability determinations. Hence, this study compares the two chemically different organogelators at three different addition levels during storage with each other and with a commercial margarine product to find out the most suitable preparations for a spreadable (breakfast margarine-like) product. Since a spreadable olive oil would produce new and unique consumption habits in olive oil preferring populations, the results of this study would be effective. Hence, the objectives of this study together with the experimental factors are novel.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Virgin olive oil (VOO) was purchased from local markets. Carnauba wax (CW) 5023 was purchased from KahlWax (Kahl GmbH & Co.,

Trittau, Germany). It is a yellow to brown solid powder/flakes with a faint odor and a 78–88 °C melting range. The producer has declared that it is safe and food grade. Monomuls® 90-35 Saturated Monoglyceride (MG) was purchased from BASF Co. (Illertissen, Germany). It is a white, tasteless, scentless microgranular solid with a minimum 90% monoglyceride, based on hydrogenated palm oil (EEC-no. E 471, FDA-CFR-no. 184.1505) and has a 64–68 °C melting range. The producer has stated that its ingredients meet the general and specific requirements for purity of the WHO/FAO-standards and directives of the EEC. Commercial breakfast margarine (BM) was purchased from a local store. It includes a 59% vegetable oil mixture, of which 20% is monounsaturated, 15% is polyunsaturated, 24% is saturated fats. It is classified as *trans* acid free with less than 1% *trans* fatty acids. All other chemicals were of analytical grade and purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, ABD).

## 2.2. Oleogel preparation

VOO oleogels with the two organogelators (CW and MG) were prepared at three different addition levels (3, 7 and 10% w/w). The decision of the selected levels was based on pre-experiments to determine the most suitable oleogels as spreadable products. To do this, the measured properties of the oleogels were compared with those of commercial breakfast margarine (BM). Previously determined amounts of VOO and each organogelator were set to isothermal temperature in a water bath at 90 °C, and then mixed thoroughly for 5 min. Finally, the hot mixture was filled into tubes and plastic cups for subsequent analyses. After overnight setting at room temperature, the oleogels were completely formed and then analyzed. For the storage study, the samples were stored at room temperature (20 °C) or in the refrigerator (4 °C) and analyzed each month. The pictures of the developed oleogels are shown in Fig. 1. The names of the different samples in this manuscript are

abbreviated as: VOO-virgin olive oil; CW-carnauba wax; MG-monoglyceride; BM-breakfast margarine; OC3, OC7, and OC10-oleogels of VOO and CW at 3, 7 and 10% addition levels; OM3, OM7, and OM10-oleogels of VOO and MG at 3, 7 and 10% addition levels.

## 2.3. Physical measurements

The instrumental color values ( $L$ ,  $a^*$  and  $b^*$ ), oil binding capacity (OBC), crystal formation time (CFT) and solid fat content (SFC) were measured according to the techniques described in our previous article (Öğütçü and Yılmaz, 2014).

## 2.4. Thermal characterization

The onset temperature, peak temperature and enthalpy of the samples for both crystallization and melting were measured by a Perkin-Elmer 4000 Series Differential Scanning Calorimetry (DSC) (Groningen, The Netherlands) equipped with Pyris 1 Manager Software according to a previously described technique (Öğütçü and Yılmaz, 2014). Briefly, a hermetically sealed oleogel sample was first heated from room temperature to 140 °C at a 10 °C·min<sup>-1</sup> heating rate and then cooled to -20 °C at a 10 °C·min<sup>-1</sup> cooling rate and kept at that temperature for 3 min for full crystallization. Finally the sample was heated again to 100 °C at a 5 °C·min<sup>-1</sup> heating rate. A sample DSC curve is shown in Fig. 2.

## 2.5. Textural characterization

As the most important textural parameters, the firmness and stickiness of each oleogel sample and the BM sample were measured with a Texture Analyzer TA-XT2i (Stable Microsystems, Surrey, UK) equipped with a custom-built block and 45° conic acrylic probe and Texture Exponent v.6.1.1.0 software (Stable Microsystems) each month during the storage period following the method described in Öğütçü and Yılmaz (2014).

## 2.6. Morphological characterization

The crystal structures of the oleogels were viewed with an Olympus B×51 (Olympus Optical Co., Ltd., Japan) polarized light microscope (PLM). The PLM pictures of the samples were taken with a CCD color video camera (Canon) attached to the microscope (Dassanayake *et al.*, 2009). The polymorphic crystal forms were measured with a Rigaku D-Max Rint 2200 model (Rigaku Int. Corp, Tokyo, Japan) X-Ray Diffractometer, equipped with a Cu source X-ray tube ( $\lambda=1.54056$  Å, 40 kV and 40 mA) and MDI Jade 7 software (Materials Data Inc, Livermore, USA) through scanning angularly from 2.0° to 50° (2 $\theta$ ) at a 2°·min<sup>-1</sup> scan rate (Öğütçü

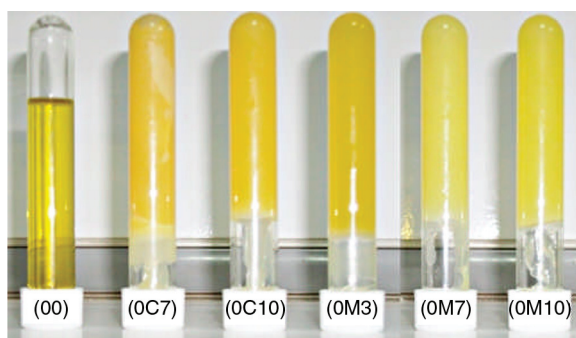


FIGURE 1. Virgin olive oil oleogels.

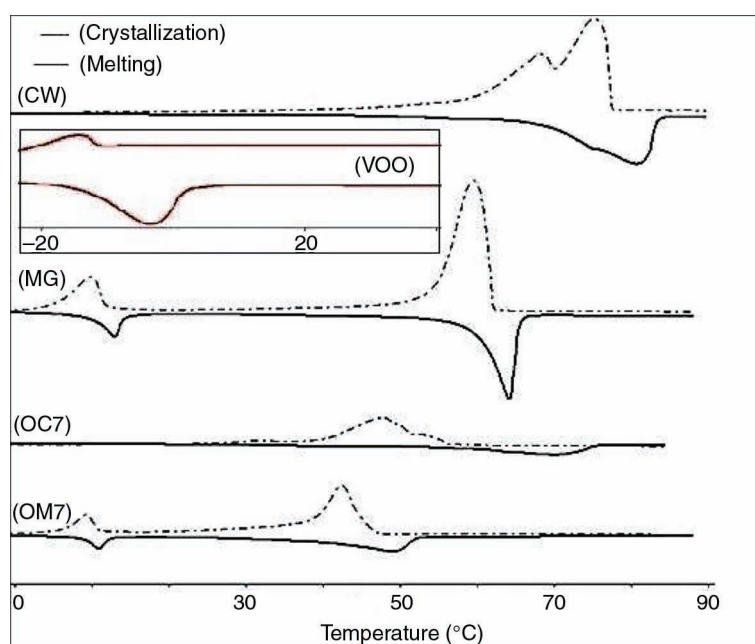


FIGURE 2. DSC patterns of crystallization and melting for VOO, CW, MG and oleogel samples.

and Yılmaz, 2014). To observe the presence of any hydrogen bonding in the oleogel samples, the infrared spectra of the samples were measured at 4000–550  $\text{cm}^{-1}$  wave range using a Perkin Elmer FT-IR Spectrum One (Perkin Elmer, Inc., US) instrument equipped with a universal ATR sampling accessory.

### 2.7. Oxidation stability determination

The oxidative stability of the stored samples was measured each month by the peroxide value (Cd 8-53 method) measurement (AOCS, 1987).

## 3. RESULTS AND DISCUSSION

The physical properties of the oleogel samples are given in Table 1. Compared to BM, the luminosity (L value) of all oleogels was much lower, since stock oil, VOO, is natural and unrefined oil, and contains some color pigments. Furthermore, because margarines are emulsion products, their color is usually naturally whiter than that of liquid oils. The  $a^*$  and  $b^*$  values of the oleogels increased as the addition level of the organogelator increased due to the natural colors of the waxes. Those two color parameters were more similar to those measured for the BM sample. The color of any oleogel sample can be adjusted by adding some oil soluble food pigments into the oil, if desired. The oil binding capacities (OBC) of the oleogels were measured by centrifuging (9167 g for 15 min) a known amount of sample, then draining the liquid oil out,

and calculating according to the equation given in Ögütçü and Yılmaz (2014). The OBC was found to be affected by the level of added organogelators, respectively. Generally, MG was better than CW for OBC. As a measurement of oil entrapment ability, OBC could be important for the perceived texture, spreadability and stability of the oleogels (Co and Marangoni, 2012). When a margarine or similar product is applied in a thin layer onto a surface, it can sometimes soften. This is usually an unwanted situation (Moskowitz, 1987). If OBC were lower it would be more probable to soften an oleogel sample (Co and Marangoni, 2012; Da Pieve *et al.*, 2010). The OBC of MG in cod liver oil organogel is reported (Da Pieve *et al.*, 2010) in % oil release as a function of a shear applied, and it was indicated that as the applied shear rate increases, oil release increases. Crystal formation time (CFT) can also give a clue about the gelation ability of an organogelator molecule. At a 3% addition level, CW could not create a stable gel, while MG formed it after 23.50 min at the same concentration. As the concentration of organogelator increases, the CFT decreases, respectively. There were no big differences for the CFT at 7 and 10% levels of CW and MG oleogels. A gelation time of 13.5 min at 4% CW in olive oil is reported (Dassanayake *et al.*, 2009). Solid fat content (SFC) is a very important criterion in hardfat stocks for both technological features and nutritional values. The SFC in the oleogel samples was usually lower in CW oleogels than that of the MG oleogels at 20 and 35 °C. In fact, at higher temperatures, it was



TABLE 1. Some physical properties of the virgin olive oil oleogels

Sample	L	a*	b*	OBC (%)	CFT (min)	SFC 20 °C (%)	SFC 35 °C (%)
OC3	41.73±0.15	-5.60±0.06	16.48±0.23	40.82±5.29	—	2.68±0.17	2.78±0.13
OC7	50.58±0.18	-6.37±0.18	22.96±0.07	71.70±1.60	10.50±0.50	5.93±0.08	5.99±0.11
OC10	54.46±0.34	-6.21±0.22	25.22±0.33	93.41±0.42	7.50±0.50	8.45±0.06	8.19±0.03
OM3	35.49±6.02	-3.48±2.45	10.43±3.57	62.31±0.47	23.50±1.50	2.78±0.08	1.08±0.01
OM7	43.09±6.65	-5.60±2.66	15.23±2.89	80.72±5.34	8.00±0.00	5.54±1.18	3.01±0.12
OM10	44.95±7.89	-5.99±2.75	16.06±2.94	99.87±0.07	7.50±0.50	9.38±0.03	4.75±0.09
BM	87.23±1.57	-2.51±0.01	10.66±0.61	—	—	12.15±0.04	—

much lower in all samples. Most importantly, the SFC in all oleogel samples was well below the addition levels of the organogelators. Hence, it could be claimed that at the given temperatures, even some of the organogelators are in liquid state. It is well established in the literature (Co and Marangoni, 2012) that organogelation could not enhance the SFC of the oil. The BM had 12.15% SFC at 20 °C, as measured. Even though this sample is an emulsion product containing nearly 40% water, the oil phase still contains more solid fat than the oleogels developed. Hence, oleogels with similar texture and much lower saturated fats can be a much healthier alternative as spreadable products.

In order to compare with the BM and select the most similar or suitable one among the oleogels developed, the thermal properties were also measured, and the results are presented in Table 2. Melting temperature is essentially the most important measure for the plastic fat products. The CW oleogels of VOO had peak melting points between 65.83 and 76.00 °C, while MG oleogels showed a greater range from 12.29 to 51.77 °C. The peak melting temperature for the commercial BM sample was measured as 47.11 °C for the oil continuous medium. Clearly oleogels of MG are more similar to BM for the melting and crystallization temperatures (Table 2). Although the producer specified 64–68 °C melting range for the MG, we measured two different melting points at 13.20 °C and 65.83 °C. Obviously the MG includes high and low melting fractions, as it is a two-component mixture. The large difference between the two measured melting temperatures can indicate that there is a lower melting point component in the Monomuls® 90-35 Saturated Monoglyceride, since the DSC melting curve yields two separate enthalpy curves. The two melting fractions were also evident in all oleogels made up with MG as organogelator. Cod liver oil and MG organogels at 7% addition level had a 53.2 °C melting temperature and 12.9 J·g<sup>-1</sup> transition enthalpy value (Da Pieve *et al.*, 2011). Although we compare VOO oleogels with a commercial BM, it should never be forgotten that margarine is an emulsion product which includes a water phase and

several other ingredients. On the other hand, oleogels are anhydrous products, but their plastic behavior and melting behavior resembles margarines and/or spreads. Hence, one would expect acceptable consumptions of VOO oleogels as breakfast margarine-like or spreadable products. Consumers would always prefer a healthy oil (Boskou, 1996), and therefore a spreadable type of VOO can promote new consumption habits. This expectation was our objective to compare the samples in order to find out the most similar oleogel sample. The melting range is critical for high quality table margarines. It should melt quickly with a cooling sensation on the palate. The heat of melting yields this cooling sensation and helps taste buds to receive the flavor. There should be no lingering greasiness or coating on the tongue. Especially for spreads or breakfast type margarines, oil separation or oiling out is an important problem caused by insufficient crystal size or character to enmesh all liquid oils (Chrysam, 1996). Since oleogels are unhydrous products, there would not be an emulsion breaking problem, but oiling out can occur and has been reported for olive oil-MG organogels under shear (Ojijo *et al.*, 2004). Hence, OBC and CFT might also be important parameters in the selection of better organogelators.

Spreadability is one of the most important attributes of margarines (Chrysam, 1996). It can be estimated by firmness (hardness) and stickiness (adhesiveness) measurements. Firmness is defined as the force required to create a given deformation under given conditions, and stickiness is defined as the force needed to pull out or remove the probe or knife from the sample. Spreadability can implicitly be estimated from both firmness and stickiness (Moskowitz, 1987). Higher correlations between hardness and spreadability, and cohesiveness and spreadability were measured, but the correlation between adhesiveness and spreadability was low in table fats (Glibowski *et al.*, 2008). Spreadability is usually defined as the easiness of a sample to be applied in a thin, even layer on a surface. Generally moderate levels of firmness and/or stickiness indicate good spreadability, since it would be very difficult to spread too firm or too sticky samples onto

TABLE 2. Thermal properties of the virgin olive oil oleogels

Sample	Crystallization			Melting		
	Onset <sub>c</sub> (°C)	Peak <sub>c</sub> (°C)	$\Delta H_c$ (J·g <sup>-1</sup> )	Onset <sub>m</sub> (°C)	Peak <sub>m</sub> (°C)	$\Delta H_m$ (J·g <sup>-1</sup> )
VOO	-13.49±0.49	-17.19±0.19	-6.15±0.15	-12.65±1.46	-3.96±0.46	71.36±1.13
CW	77.87±0.12	75.04±0.70	-183.81±5.64	68.78±0.19	76.30±0.05	199.68±13.04
MG	11.16±0.89	10.14±0.12	-23.27±3.08	10.62±0.10	13.20±0.02	24.20±1.04
(Fr2) <sup>a</sup>	63.83±0.03	61.17±0.02	-105.71±9.47	61.72±0.15	65.83±0.19	103.97±6.42
BM	19.42±0.74	16.91±0.75	-2.89±0.13	35.36±0.01	47.11±0.00	94.19±2.51
OC3	63.83±0.03	61.17±0.02	-105.71±9.47	61.72±0.15	65.83±0.19	103.97±6.42
OC7	53.57±1.54	50.77±0.49	-11.08±0.44	63.37±0.26	71.81±2.72	12.05±0.12
OC10	56.78±0.56	51.75±0.00	-15.51±0.30	63.08±0.45	76.00±0.13	14.81±1.56
OM3	12.66±0.14	11.08±0.18	-0.44±0.05	10.69±0.38	12.56±0.35	0.49±0.02
(Fr2)	36.97±0.48	34.83±0.91	-1.74±0.17	31.06±0.49	39.58±0.38	1.45±0.15
OM7	12.75±0.20	11.17±0.08	-1.30±0.09	10.83±0.62	12.69±0.11	1.25±0.01
(Fr2)	45.17±0.30	41.96±0.45	-5.42±0.34	38.32±0.93	48.70±0.25	4.87±0.25
OM10	12.41±0.17	10.84±0.09	-2.04±0.15	10.74±0.08	12.29±0.33	2.11±0.19
(Fr2)	49.00±1.47	45.80±1.28	-7.66±0.07	43.35±0.79	51.77±0.44	6.49±0.07

<sup>a</sup>Fr2 : fraction two.

a surface. For both measurements, the temperature of the measurement is critical and must also be reported (Moskowitz, 1987). Sometimes SFC is correlated with spreadability, but it may not correlate well with firmness for most margarine since the nature of fat crystals is also a determining factor. Solid fat index values of 10-20% were found optimal at serving temperatures for consumer panel values of margarine spreadability. In addition, it was stated that not only spreadability but also smoothness and brittleness are dependent on crystal nature (Chrysam, 1996).

The firmness values of the VOO oleogels are shown in Fig. 3. For samples stored at both 4 and 20 °C, the firmness values of CW oleogels were always higher than those of the MG oleogel samples. During the 90 days storage, the firmness values of the MG oleogels at the two storage temperatures were gradually decreased, while there was no big decrease in the CW oleogels. Since MG oleogels are based on saturated monoglycerides as organogelators, it would be quite possible that storage temperature affects the softening behavior of the monoglyceride and hence the oleogel firmness is strongly affected. The difference between 3% and 10% addition levels for the firmness of CW was significantly greater than that of the difference for the MG oleogels. Among all the developed and stored oleogel samples, the range of firmness was from the lowest of 6.99 g for 3% CW containing a sample stored at 20 °C for 90 days to the highest of 728.75 g for 10% CW containing a sample stored at 4 °C for 60 days. The range of firmness for the commercial BM sample was from the lowest of 67.57 g for the sample stored at 20 °C

for 30 days to the highest of 370.93 g for the sample stored at 4 °C for 90 days. Clearly most of the oleogels containing around 7% organogelator had firmness values within the firmness value range of the commercial BM sample. In fact, the firmness values

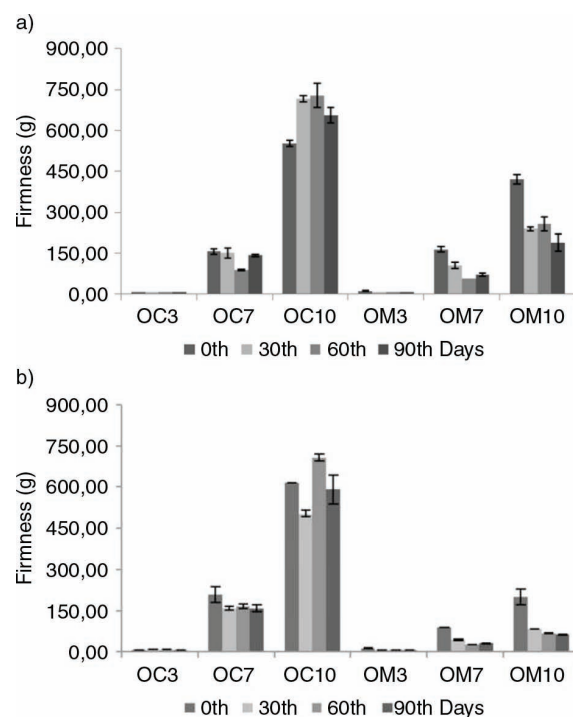


FIGURE 3. Firmness values of the virgin olive oil oleogels stored for 90 days at (a) 4 °C, (b) 20 °C.

of the other oleogels were not very different. Similar trends in changes were also evident for the stickiness values of the oleogel samples. At both storage temperatures, the stickiness of the corresponding CW oleogels was higher than that of the MG oleogels. While the stickiness of the MG oleogels decreased during storage, the change was unidirectional and small for the CW oleogels. Also, the stickiness of the refrigerator stored samples was higher than that of their room temperature stored counterparts. The lowest stickiness was with the 3% MG containing the sample stored at 20 °C for 90 days, while the highest stickiness among all the oleogels developed was with the 10% CW containing the sample stored at 4 °C for 60 days. The range of the measured stickiness for the BM sample was from 33.84 g stored at 20 °C for 30 days to 199.40 g stored at 4 °C for 90 days. From these texture parameters, it can be said that the spreadability of the VOO oleogels is quite similar to the commercial breakfast margarine sample. Especially, the MG oleogel at 7% addition level yielded very similar texture results. The other samples were not very different, and can be adapted as spreadable products. Of course, more studies for sensory properties and consumer perceptions are needed and will be carried out in our laboratory.

The crystal morphology of the oleogel samples was also investigated to gain more information about the texture and hence the stability.

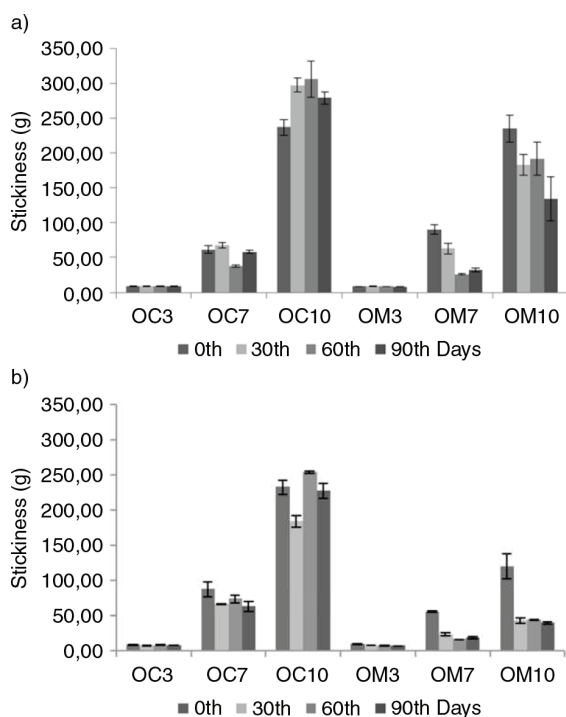


FIGURE 4. Stickiness values of the virgin olive oil oleogels stored for 90 days at (a) 4 °C, (b) 20 °C.

The PLM pictures are shown in Fig. 5. The CW oleogels included dense and crowded rod-like crystals. A very similar crystal structure was shown by Dassanayake *et al.* (2009). They compared the CW crystal with rice bran and candelilla wax crystals, and reported needle-like structures for all three. In fact, in this study and in their study, the crystals of CW are a little different than the true needle-like crystals of rice bran wax (Dassanayake *et al.*, 2009) or sunflower wax (Hwang *et al.*, 2012). Instead, we would name it as short rod-like aggregates. On the other hand, the MG crystals are absolutely rosette-like or spherulitic as reported by Kesselman and Shimoni (2007) for corn oil-MG organogels. In contrast, in the same study (Kesselman and Shimoni, 2007), needle-like crystals were reported for virgin olive oil-MG organogels. Obviously, MG can form needle-like or rosette-like crystals, and the reason behind this phenomenon needs further investigation. In order to determine the polymorphic nature and sub-cell type of the crystals, the X-ray diffraction (XRD) patterns of all oleogel samples together with the CW, MG and BM were measured and the results are given in Table 3. To show the patterns graphically, the sample curves are presented in Fig. 6 for the OC10, OM10 and BM samples. The wide-angle diffraction peaks of 3.74 and 4.16 Å for the OC10 sample (Fig. 6a), and similar peaks listed in Table 3 for the CW oleogels indicate an orthorhombic perpendicular sub-cell packing of the crystals, as suggested by Dassanayake *et al.* (2009) for the carnauba wax-salad oil organogels. It was shown that CW organogels having the 0.415 and 0.373 nm peaks are similar to those observed in the  $\beta'$  polymorphs of triacylglycerol crystals. It is also stated that  $\beta'$  crystals are characterized by a smooth texture and better mouthfeel in margarine and shortening products (Dassanayake *et al.*, 2009), and very smooth and homogenous texture was also determined for the CW and MG oleogels of VOO in this study. There are more peaks at the wide-angle and small-angle regions of the OM10 sample (Fig. 6b) than those of the OC10 sample (Fig. 6a). Wide-angle region diffraction peaks from 3.34 Å to 4.57 Å, and also small-angle region peaks at around 7.99 to 43.51 Å for the MG oleogels were determined (Table 3). Very similar peaks were shown for 5% MG in cod liver oil organogels (Da Pieve *et al.*, 2010) and for 7% MG in cod liver oil organogels (Da Pieve *et al.*, 2011). The diffraction peaks of only MG, CW and BM samples were also measured and presented in Table 3. Clearly, the diffraction peaks of the waxes in bulk and in oleogels are quite similar, respectively. The peaks for the commercial BM sample (Fig. 6c) seem very similar to that of the MG oleogel sample (Fig. 6b). Hence, the higher textural similarity between the two samples can be explained by the high level of similarities between



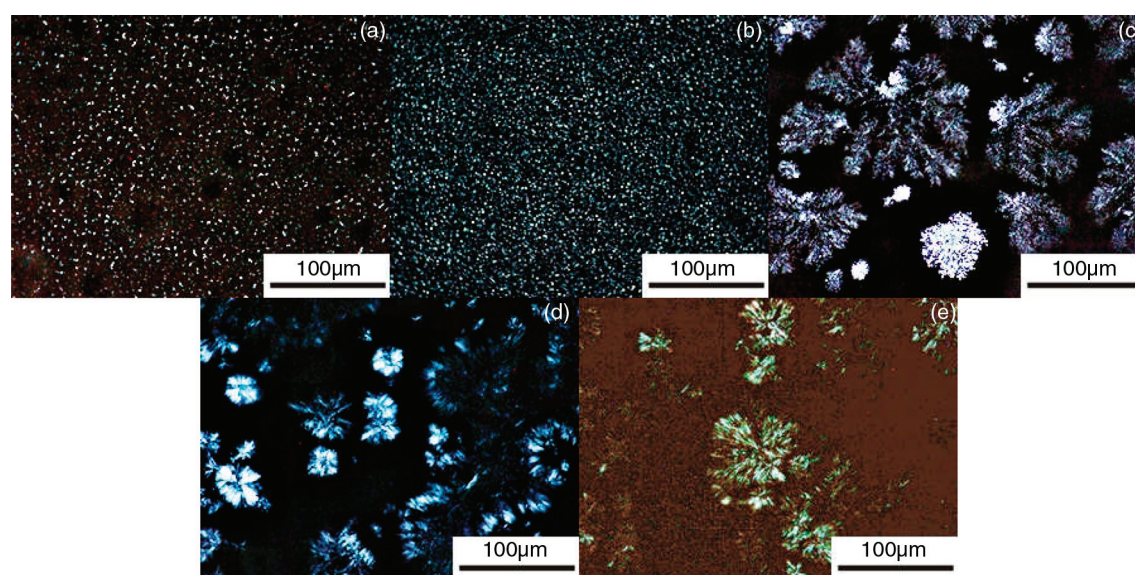


FIGURE 5. Polarized light microscopy pictures of the virgin olive oil oleogels, (a) OC7 (b) OC10 (c) OM3 (d) OM7 (e) OM10.

the wide-angle and small-angle region diffraction peaks of the crystals present. In fact, CW oleogels were not different, but rather were less similar than that of the MG oleogels (Fig. 6 and Table 3). For all samples, it was also evident that intensities of the wide-angle and small-angle regions were very different, indicating strong anisotropy in the crystal growth rates. It can also be observed that the MG oleogel and BM sample include lamellae with a 43.51 and 41.23 Å width. The broad range of diffraction peaks from around 4.16 to 24.60 Å is due to the amorphous scattering of the triacylglycerols of the entrapped liquid oil comprising at least 90% of the oleogel samples. From these results, it can be concluded that both MG and CW oleogels of VOO are very smooth, homogeneous and creamy, just like the  $\beta'$  crystals of triacylglycerols created

by cooling and tempering processes. The presence of some intermolecular hydrogen bonding in the MG organogelator and MG oleogel samples were determined by FT-IR measurements and the spectra are presented in Fig. 7. There is a similar study in the literature (den Adel *et al.*, 2010) showing the FT-IR spectra of  $\beta$ -sitosterol+ $\gamma$ -oryzanol organogels. Based on their findings and suggestions, we also suggest the presence of some weak intermolecular hydrogen bonding in the MG oleogels evident from the deformations in the 3300-3400  $\text{cm}^{-1}$  wave number range bands (Fig. 7).

The oxidative stabilities of the oleogel samples and BM sample were monitored for 3 months at room and refrigerator temperature storage (Fig. 8) by monthly peroxide value (PV) measurements. Among all oleogel samples, the lowest PV (1.00

TABLE 3. X-ray diffraction patterns of the virgin olive oil oleogels.

Sample	2- Theta	d (Å)
CW	4.83, 19.37, 21.53, 23.81, 30.02, 36.29, 40.49, 43.80	18.27, 4.57, 4.12, 3.73, 2.97, 2.47, 2.22, 2.06
MG	3.52, 5.56, 7.41, 10.10, 11.14, 19.52, 20.49, 22.76, 23.59, 8.72, 36.78, 39.69, 42.12	25.02, 15.88, 11.95, 8.75, 7.93, 4.54, 4.32, 3.90, 3.76, 3.10, 2.44,
BM	2.14, 4.02, 6.32, 19.26, 23.24	41.23, 21.95, 13.96, 4.60, 3.82
OC3	—	—
OC7	4.41, 19.34, 21.43, 23.78, 27.89,	19.98, 4.58, 4.14, 3.73, 3.19,
OC10	3.83, 19.25, 21.34, 23.74, 29.86, 36.00	23.00, 4.60, 4.16, 3.74, 2.26, 2.14, 2.98, 2.49
OM3	2.02, 4.38, 7.58, 19.54, 23.52, 26.60	43.50, 20.15, 11.65, 4.53, 3.77, 3.34
OM7	2.02, 3.58, 5.52, 7.31, 10.99, 19.37, 20.32, 22.73	43.51, 24.64, 15.99, 12.06, 8.04, 4.57, 4.36, 3.90
OM10	2.02, 3.96, 5.40, 7.34, 11.06, 19.39, 20.32, 22.70, 23.43, 36.71	43.51, 22.26, 16.34, 12.03, 7.99, 4.57, 4.36, 3.91, 3.79, 2.44



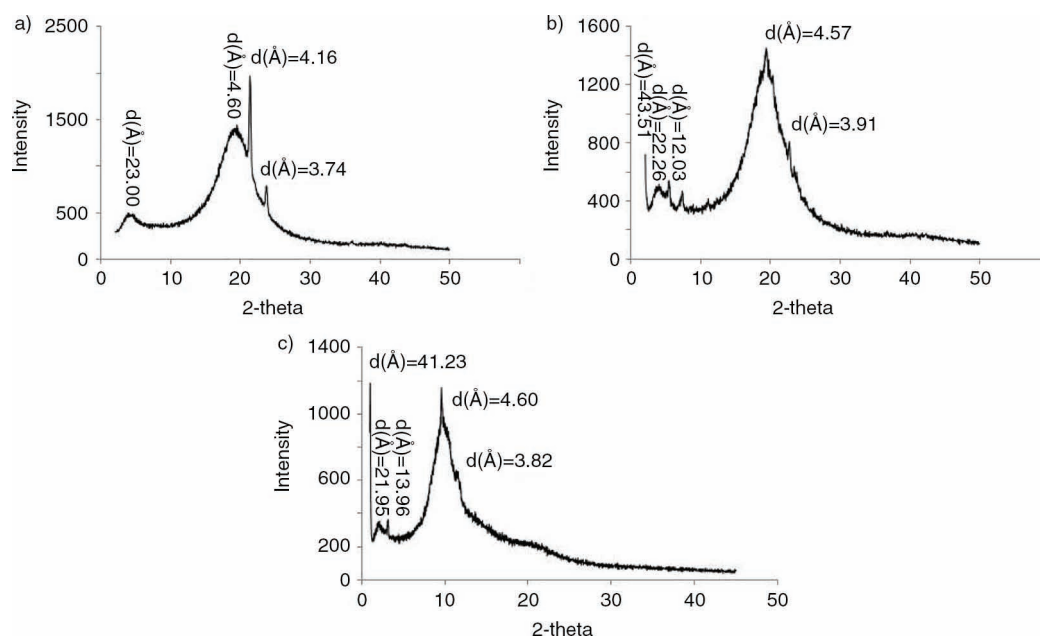


FIGURE 6. X-RD patterns of the virgin olive oil oleogels, (a) OC10 (b) OM10 (c) BM.

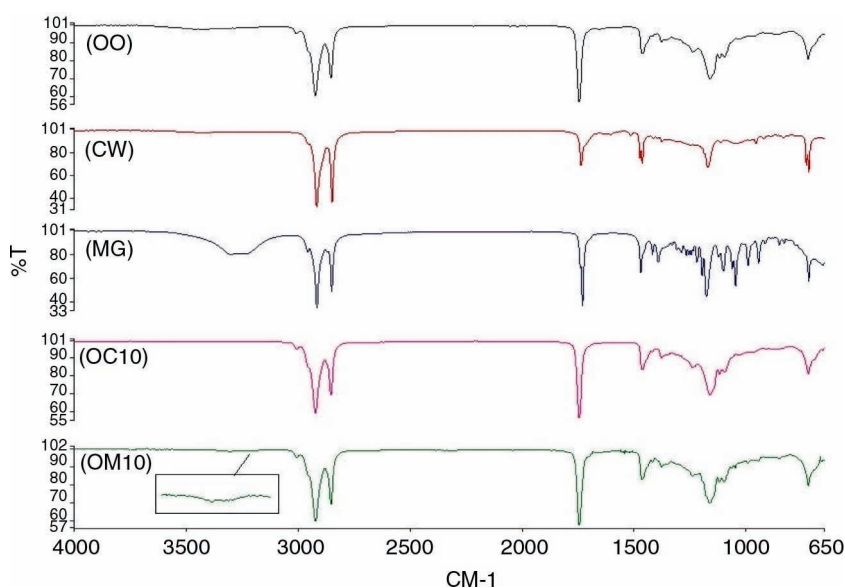


FIGURE 7. FT-IR spectra of the virgin olive oil oleogels.

$\text{meqO}_2 \cdot \text{kg}^{-1}$ ) was measured in the 7% MG containing the sample stored at 4 °C for 0 days, and the highest PV ( $1.96 \text{ meqO}_2 \cdot \text{kg}^{-1}$ ) was measured in the 7% MG containing sample stored at 20 °C for 90 days. In addition, the range for the BM sample was from  $0.05 \text{ meqO}_2 \cdot \text{kg}^{-1}$  for the sample at the beginning of the storage at 4 °C to  $1.21 \text{ meqO}_2 \cdot \text{kg}^{-1}$  for the sample stored for 90 days at 20 °C. In general, there were no significant differences between the

two storage temperatures for the measured PVs of the corresponding samples, while there was a slow, gradual increase in the PVs throughout the storage time at both temperatures. The measured PV of all oleogel samples were well below  $2 \text{ meqO}_2 \cdot \text{kg}^{-1}$ , indicating the good oxidative stability of the samples. Since no antioxidant additive was added to the samples, the observed oxidative stability is due to the natural antioxidant compounds

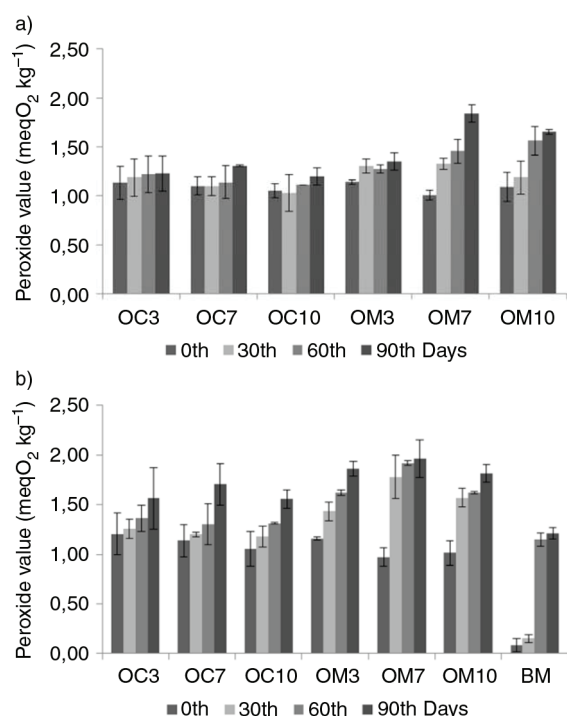


FIGURE 8. Peroxide values of the virgin olive oil oleogels stored for 90 days at (a) 4 °C, (b) 20 °C.

(tocols, polyphenols and sterols) found in the virgin olive oil. Obviously, oleogelation has not created any degradation to the antioxidant compounds, which can be included as another advantage of the technology.

#### 4. CONCLUSIONS

This study has proven that breakfast margarin-like or spreadable products of VOO can be produced by organogelation technology with two different types of organogelators, namely carnauba wax and monoglyceride. Since VOO is a very healthy and preferred oil, plastic, creamy, spreadable types of VOO can help to promote new consumption habits for consumers. The results have shown that especially the 7% MG containing oleogel, but also in fact all oleogels developed can resemble the textural and thermal properties of commercial breakfast margarine. The oxidative stability of the developed oleogels was also very good. Hence, the oleogels which can be spread on to a slice of bread would be a very novel form of consumption for VOO consumers.

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